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Résumé : Nous avons étudié l'émission d'ions négatifs à partir de cibles solides organiques bombardées par des ions moléculaires et des agrégats atomiques. Nous présentons ici les résultats obtenus avec une cible de phenylalanine. Nous avons utilisé les projectiles organiques de masse 73 $[Si(CH_3)_3]^+$, 147$[Si(CH_3)_3OSi(CH_3)_2]^+$, 300 [ion moleculaire du coronène $C_{24}H_{12}]^+$, 598 [le dimère du coronène $2(M-H)]^+$ et les ions atomiques et polyatomiques de masse 133 $[Cs]^+$, 393 $[Cs_2I]^+$, 653 $[Cs_3I_2]^+$. Ces ions primaires ont été produits en bombardant une cible de coronène et de CsI par des produits de fission du ^{252}Cf. Ensuite ces ions ont été accélérés et focalisés sur l'échantillon à étudier. Des mesures de temps de vol sophistiquées des ions primaires et secondaires ont été exécutées avec un système d'acquisition de données spéciales. Tous les temps de vol ont été enregistrés simultanément.
Le rendement des ions moléculaires de phenylalanine a été étudié en fonction de l'énergie et de la masse des projectiles. Une grande augmentation du rendement est observée avec l'énergie et la masse.

Abstract : We have studied the negative secondary ion emission from solid organic targets bombarded by molecular ions and cluster ions. As an example we present here the results obtained with the compound phenylalanine. We have used organic projectiles of mass 73 $[Si(CH_3)_3]^+$, 147$[Si(CH_3)_3OSi(CH_3)_2]^+$, 300 [molecular ion of coronene $C_{24}H_{12}]^+$, 598 [coronene dimer $2(M-H)]^+$, and atomic and polyatomic ions of mass 133 $[Cs]^+$, 393 $[Cs_2I]^+$, 653 $[Cs_3I_2]^+$. These primary ions have been produced in the bombardment of targets of coronene and CsI by fission fragment from a ^{252}Cf source. They were accelerated and focussed on the sample target. Sophisticated time of flight measurements of the primary and secondary ions have been performed with a special data acquisition system. All the time of flight mass spectra were recorded at one.
The secondary molecular ion yield of the phenilalanine $(M-H)^-$ = 164 has been studied as a function of the energy of impact and of the mass of the projectile. A large enhancement of the yield with the mass and the energy is observed.

INTRODUCTION

Recently there has been much interest in the secondary ion emission from materials induced by cluster ion bombardment /1/. The incident cluster ions have velocities in three different regimes : greater than the Bohr velocity, v_o = 0.22 cm/nsec (fast), approximately equal to v_o, and much less than v_o (slow). The reason for the interest in cluster induced ion emission is the increased secondary ion yields when compared with single atom ion projectile yields of the same charge state. In this paper, we describe the experimental procedure for obtaining quantitative yields of negative ions desorbed by slow (keV) incident positive cluster ions and we present some recent results for the yield of an organic compound phenylalanine desorbed by the molecular ion of coronene and by CsI cluster ions.

EXPERIMENTAL

The experiments were performed at the Institut de Physique Nucléaire in Orsay, France. The experimental approach for generating and accelerating various cluster ions for use as projectiles is described elsewhere /2/. Briefly, the cluster ions (as well as single atom ion species) are produced by fission fragment induced desorption from the appropriate material deposited on a metallic surface (aluminized mylar). This surface is at a positive potential U_1. The desorbed ions (called primary ions in the following) are accelerated by an extraction grid at ground and travel in a field free region of 15 cm. At the end of this region the primary ions bombard a sample surface titled by 20° with respect to the primary beam direction ion. Under impact, electrons and negative ions are emitted from the surface (biased at a negative potential U_2), accelerated into a second field free region, and detected by a set of channel plates (CEMA2 in Fig. 1). The start signal is given by the complementary fission fragment in the detector CEMA1.

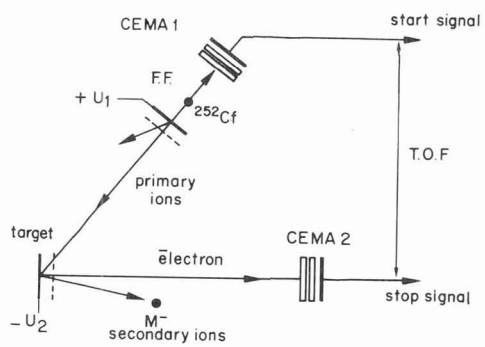

Figure 1 : Experimental set up.

The electrons are used as stop signals for the primary ion time of flight (TOF) measurements. In addition the stop signals generated by the secondary negative ions are also recorded. The spectrum shown in Fig. 2a, measured with the IPN multistop time-to-digital converted (TDC), is therefore the sum of two time of flight (TOF) spectra :

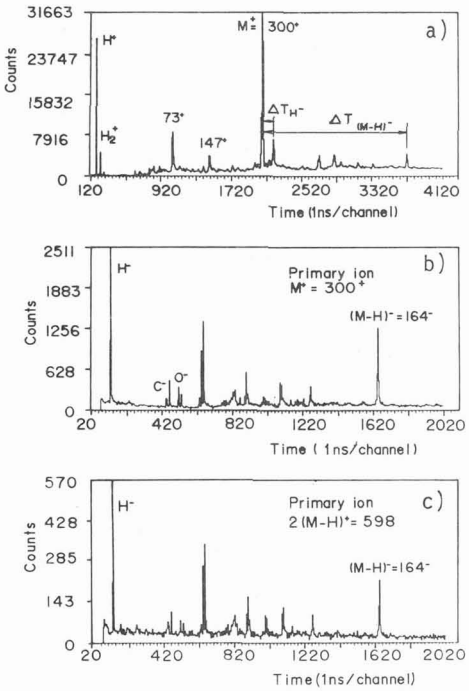

Figure 2 :

a) Total TOF spectrum : primary ions from a coronene target and secondary ions from a phenilalanine target (see text).

b) Secondary ion TOF spectrum generated by the impact of mass M^+=300 on the phenilalanine target. A coincidence time window has been set (on mass 300) in the spectrum 2a.

- the TOF spectrum of the primary ions (start with fission fragments from ^{252}Cf and stops from electrons),
- the TOF spectrum of the secondary ions (same start and stops from secondary ion impacts on CEMA2).

The first part of the TOF spectrum looks like a regular TOF spectrum of coronene desorbed by fission fragments with the presence of the peaks H^+, H_2^+, H_3^+... M^+ = 300 and $2(M-H)^+$ = 598. However almost every peak can be considered as a time origin for the secondary ion time of flight spectrum. For example, the first peak after M^+ = 300 corresponds to the emissions of H^- ions due to the impact of M^+ = 300 on the phenylalanine sample. The time difference between M^+ = 300 and another peak (see Fig. 2a) in the spectrum allows also to identify the presence of the molecular ions of phenylalanine ($[M-H]^-$ = 164) desorbed by impact of M^+ = 300. Only a few mass assignments can be made in this way although the spectrum, which is very complex, contains much more information. Several secondary ion TOF peaks are masked by the background of the primary ion TOF.

To overcome these difficulties we have used a special data acquisition systeme described in ref/3/. A TDC event is composed of one start followed by many stops on a certain time range (8 microseconds [13 bits] in the present experiment). Anywhere in this time range, it is possible to select a time window which can be used as a time origin for time measurements with the following stop signals. The result of the time digital conversion with the new origin is stored (event by event) in a special memory and gives rise to a specific TOF spectrum. Coincidence windows can be set to a width of about 10

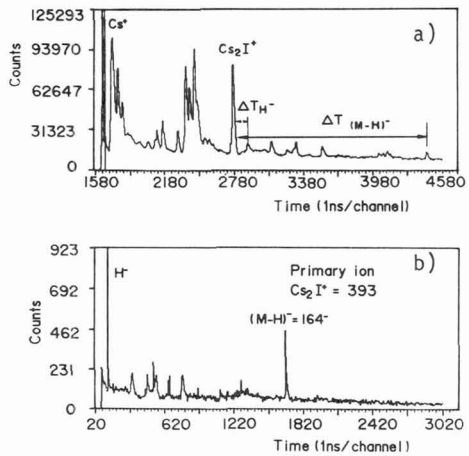

Figure 3 :

a) Total TOF spectrum : primary ions from a CsI target and secondary ions from a phenylalanine target.
b) Secondary ion TOF spectrum with a time origin corresponding to the impact of Cs_2I^+ on the sample.

channels on any peak of interest in the total TOF spectrum. By this coincidence counting method, individual spectra are extracted from the total TOF spectrum in real time during the data acquisition. As examples, Figures 2b and 2c show spectra of ions desorbed from phenylalanine target due to the impact by the molecular ions of coronene (M^+ = 300) and due to the impact by the dimer ($2[M-H]^+$ = 598). the two spectra are similar but the secondary ion yields (with respect to the number of primary ions bombarding the sample) are different.

A more complex example is shown in Fig. 3a and 3b. The phenylalanine target is bombarded by cesium ions and by cesium iodide clusters (the coronene deposit has been replaced by a CsI deposit -see Fig. 1-). Fig. 3a shows a total TOF spectrum. The peaks are due to the detection of electrons as stop signals as well as secondary ions generated by impacts of Cs^+, Cs_2I^+,... and other primary ions on the phenylalanine sample. In Fig. 3b the time origin is the instant of impact of Cs_2I^+ only and the corresponding time of flight spectrum of phenylalanine is observed. The molecular ion $(M-H)^-$ of phenylalanine desorbed by Cs_2I^+ is clearly seen.

This new method of time of flight measurement allows to extract several spectra from one single spectrum. The experimental conditions are kept the same during the experiment (same target, same detection...). the secondary ion yields due to the bombardment of the target by different kinds of projectiles can be extracted from one experiment.

The emission yield for an ion of mass M is given by :

$$Y_M = (N_M - N_M[BG]) / (N_{PI} - N_{PI}[BG]) \qquad (1)$$

N_M is the number of counts in the peak of mass M in the TOF spectrum in coincidence with the primary ions.

N_M[BG] is the number of counts in the peak of mass M in the TOF spectrum measured in coincidence with a time window set on the background close to the primary ions.

N_{PI} and N_{PI}[BG] are the number of counts in the time window set on the peak and the backgroung. $N_{PI}-N_{PI}$[BG] is the number of start events for a correlated spectrum. It is assumed in relation (1) that we have single impact on the sample. This is not the case when Cs^+ ions are emitted from the CsI deposit by the fission fragments and therefore a correction must be made on the number N_{PI} to obtain the true number of primary ions of Cs^+. We have determined the number of Cs^+ emitted by fission fragments from the CsI target. The secondary ion yield of $(M-H)^-$ due to the impact of primary Cs ions has been measured as a funciton of grid transparencies with the grids set between the CsI target and the phenylalanine target. This method is sensitive and we have found a value of 2.0±0.2 ions emitted per fission fragment. This result is in agreement with the value found at Orsay /4/ and also by the Darmstadt group /5,6/.

In the present experiment the positive primary ions are accelerated in the space between the sample and the extraction grid. Therefore the angle of incidence B' varies according to the relation :

$$B' = \mathrm{Arcos}[(U_1/U_1-U_2)^{1/2}.\cos B] \qquad (2)$$

U_1 is the acceleration potential of the primary ions
U_2 is the acceleration potential of the secondary ions
B is the tilt angle between the sample surface and the direction of primary beam.

The variation of B' is relatively small under our experimental condition. It has been verified that at a constant energy of impact (by varying U_1 and U_2), the influence of the B' variation on the secondary yield is negligible.

RESULTS AND DISCUSSION

Figure 4 shows the effect of primary ion velocity on the $(M-H)^-$ yield of phenylalanine due to incident coronene molecular and dimer ions (Fig. 4a) and due to incident cesium and cesium iodide cluster ions (Fig. 4b). The x axis scale is given in keV per mass unit ($=kV^2$) and therefore comparison of secondary ion yields can be made easily at the same velocity for various projectiles. The bombarding energies ranged from 7.86 keV to 28 keV. For all curves shown, the lines drawn through the data points are to aid the eyes. Error bars for the experimental points are less than 10 % in all cases. For the experiment using coronene as the primary ion source, primary ions of mass 73 [$Si(CH_3)_3$] and mass 147 [$Si(CH_3)_3OSi(CH_3)_2$+] were also observed for their desorption efficiency. The general trend is that the yields are much greater for the higher mass projectiles. For example there is at low velocity a yield

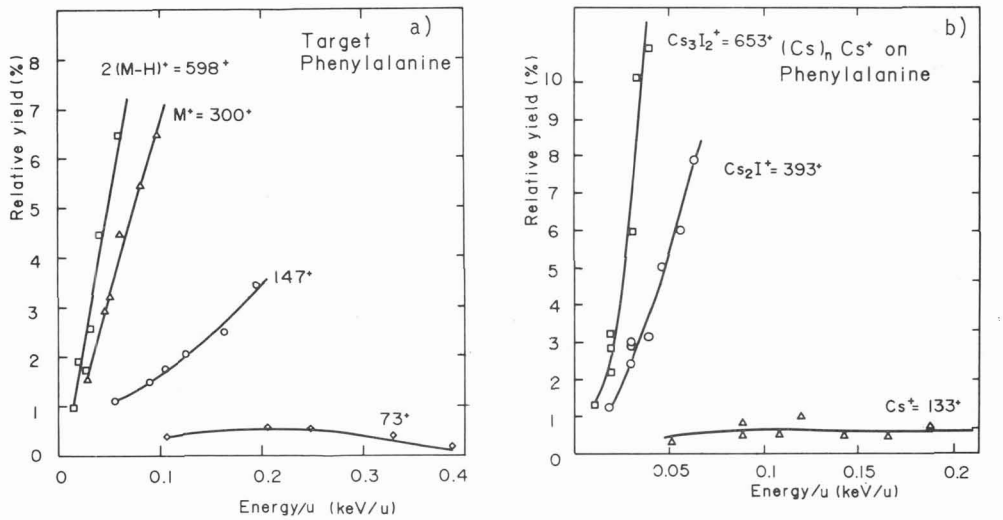

Figure 4

a) Secondary ion yield of the molecular ion $(M-H)^-$ of phenylalanine as a function of the incident mass unit ($=kV^2$) of the projectiles (coronene ions and dimers). The secondary ion yields can be compared easily at the same velocity.
b) same as above. The projectiles are Cs ions and CsI cluster ions.

enhancement by a factor of around 20 between Cs^+ and Cs_2I^+ as projectiles. For cluster ions or molecular ions the rate of increase with the projectile velocity is also very important. The observed yields for other secondary ions and the trends are the same.

CONCLUSION

The use of polyatomic ions as projectiles to induce secondary ion emission from organic solids is found to be very interesting. It is shown that single ion counting technique and coincidence methods are particularly useful for these experiments. The results presented here show that increased secondary ion yields can be achieved for the same amount of energy deposited by simply using a polyatomic, rather than a monoatomic, primary ion. It is not yet clear whether the increased yields of phenylalanine seen with the cesium iodide species and the coronene ions are due to increased mass or an increase in the number of particles in the projectile. In addition, the existence of coherent effects in the desorption process remains to be determined as the correct experimental observable remains to be identified, e.g. Y/(≠ of constituents in cluster), Y/(amu of projectile), $Y/\sum (dE/dx)_n$, etc. Further data analysis is in progress in order to understand the role of cluster velocity, mass, and constituent number in the yields of secondary ions.

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